

On the theory of lower critical solution points in hydrogen-bonded mixtures

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The theoretical description of lower critical solution points in hydrogen-bonded binary liquid mixtures has advanced significantly in recent years. However, while the decorated-lattice theories of Wheeler, *et al.*¹ and the coupled Ising–Potts models of Walker and Vause, *et al.*^{2,3} have proven to be descriptive of general and specific phase equilibria properties, they are mathematically quite complicated, and the relation of their parameters to real systems is not totally clear. The purpose of this note is to show that these systems can be described by a very simple approach which is akin to that used in the description of hydrogen bonding within the theories of helix–coil transitions.⁴ Instead of dealing with molecular orientations as fluctuating statistical variables on the same footing with the mixing degrees of freedom, one may preaverage them to arrive at statistical weights for the *two distinct* states of interacting components—bonded and nonbonded. Within this approach, the relevant thermodynamic parameters in these systems are identified more clearly than in the abstract spin models, and the simplicity of the method should allow for a straightforward inclusion of hydrogen bonding effects into studies of more complex systems.⁵

Lower critical solution points are not confined to mixtures of small molecules, but, in fact, have been observed in solutions of polar polymers^{6,7} and, to illustrate the above approach, consider the basic Flory–Huggins theory of polymer solubility.⁸ Within that theory, the free energy of mixing is given in terms of an entropy of mixing which neglects effects from specific component interactions, and an energy of mixing written in terms of the parameter $\chi \propto w/k_B T$. Here, $w = w_{ss} + w_{pp} - 2w_{ps}$, and the subscripted w 's are solvent–solvent, polymer–polymer, and polymer–solvent interaction energies. Clearly, if the w 's are temperature independent, then only an upper critical solution point is predicted. To discuss lower critical solution points, χ must be generalized to measure the *free energy* associated with interactions. In the simplest case, we include the possibility of hydrogen bonding between polymer units and solvent only. The free energy of interaction of the polymer–solvent pair is $-k_B T \ln Z_{ps}$, where

$$Z_{ps} = e^{-\beta F_{ps}^*} + e^{-\beta F_{ps}^0}, \quad (1)$$

and F_{ps}^* , F_{ps}^0 are the free energies associated with the bonded and nonbonded configurations. Thus, the generalization of the energy factor w is

$$(E_{pp}^0 - TS_{pp}^0) + (E_{ss}^0 - TS_{ss}^0) + 2k_B T \ln Z_{ps}. \quad (2)$$

The quantity $S_{pp}^0 + S_{ss}^0 - 2S_{ps}^0$ is expected to be small,

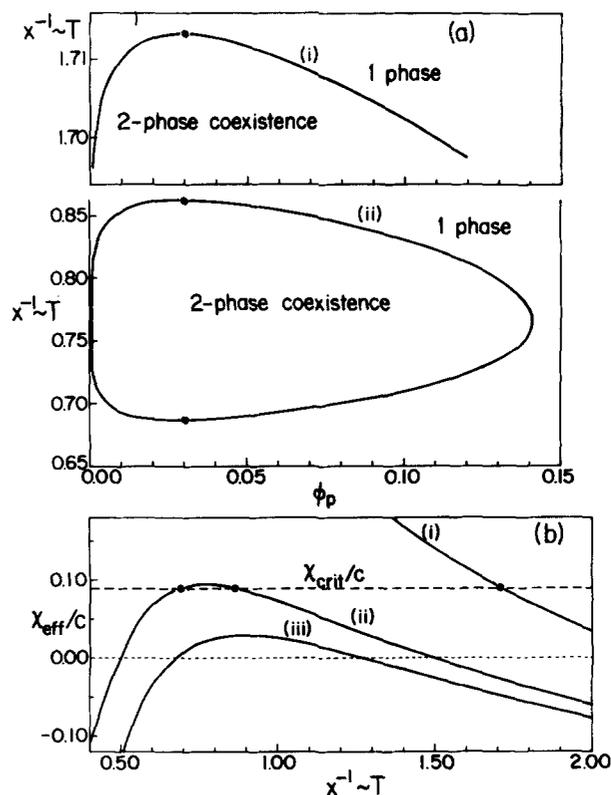


FIG. 1. (a) Temperature-composition (ϕ_p = volume fraction of polymer) phase diagrams calculated from Eq. (3) with $N = 10^3$, $c = 6$, $z = -1$, for various ratios of the energy parameters x and y . The heavy dots are the critical points. (b) Temperature dependence of the effective Flory–Huggins parameter [left-hand side of Eq. (3)] for various ratios of x to y . Labels (i) and (ii) refer to the coexistence curves in (a). Curve (iii) is for a miscible system.

since without specific interactions, little ordering occurs. Ignoring this term, we may write the criticality condition $\chi = \chi_c$ as

$$x - \ln(1 + \exp(y + z)) = \frac{1}{c} \chi_c, \quad (3)$$

where c is the coordination number,

$$x = \frac{-\beta}{2} (E_{pp}^0 + E_{ss}^0 - 2E_{ps}^0),$$

$$y = \beta (E_{ps}^0 - E_{ps}^*),$$

$$z = (S_{ps}^* - S_{ps}^0)/k_B,$$

and

$$\chi_c = (1 + N^{1/2})^2 / 2N$$

for polymers of N units. As in previous works,^{2,3} a given system is characterized by a definite value of z (entropy of

formation of hydrogen bonds) and by a ratio of energies x and y . Then, a temperature scan corresponds to moving in (x, y, z) space in a plane of constant z , from the z axis ($T = \infty$) out along a ray of fixed direction as T decreases. For appropriate values of the parameters, two solutions of Eq. (3) exist, giving both an upper and lower critical solution temperature (CST). Figure 1(a) shows typical coexistence curves obtained by the standard methods,⁸ while Fig. 1(b) displays the temperature dependence of the effective χ , obtained by using Eq. (2) in place of w . As the bonding interactions are made more favorable, a system with only an upper CST (i) evolves to form a closed loop (ii), and finally becomes completely miscible. These results are qualitatively identical to the previous lattice-gas theories,¹⁻³ but are considerably more simply derived.

Closed-loop coexistence curves have been observed in aqueous solutions of polyethylene glycol,⁶ and of vinyl alcohol-vinyl acetate copolymers,⁷ which clearly have a large amount of hydrogen bonding. In the polyethylene glycol systems, the miscibility gap grows with increasing polymer length N . Such a trend comes directly from the present calculation, since χ_c in Eq. (3) decreases with increasing N , while the interaction parameters are fixed, so that the left-hand side of Eq. (3) has the same temperature dependence for all N .

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COMMENTS

Comment on "IR-spectroscopic study of isotope effects on the NH/ND stretching bands of meso-tetraphenylporphine and vibrational hydrogen tunneling"

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In a recent paper, Limbach, Hennig, and Stulz¹ reported the IR measurement of NH/ND stretching vibration in free-base tetraphenylporphine (TPP). The observation of narrow bandwidth (20 cm^{-1}) in IR spectra lead them to conclude that the migration of inner hydrogen atoms (see Fig. 1) takes place without substantial coupling to the motion of heavy atoms (skeleton). However, this conclusion is misleading in that the bandwidth in IR spectra may not be relevant to the proton-skeleton coupling^{3,4} in the proton migration process.

At first, let me summarize the origin of A-H stretching bandwidth. Within the adiabatic approximation, in which the A-H stretching motion is separated from the slower heavy atom vibrations,² the absorption of infrared light can be described by the transitions between A-H vibrational states, which are modulated by the slow vibrations, as shown

in Fig. 2(a). It should be noted in this diagram that the effective potential along the coordinate of slow vibration is dis-

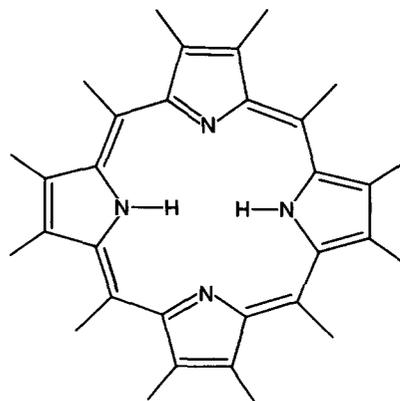


FIG. 1. One of the tautomers in free-base porphine. One of the resonance structure is also shown.